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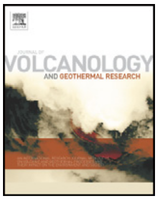

Rare earth elements in sinters from the geothermal waters (hot springs) on the Tibetan Plateau, China

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ABSTRACT

The mineralogical and geochemical composition of sinters from the geothermal areas on the Tibetan Plateau was determined. They occur as siliceous, salty and calcareous sinters but biogenic siliceous sinters were also found. The analyses indicate that there are no distinct inter-element relationships between individual rare earth elements (REEs) and other elements. Formed from the same geothermal water, the mineralogical and chemical composition of the sinters is influenced by their genesis and formation conditions. The REE distributions depend on the origin of the sinters. Fe–Mn phases in sinters tend to scavenge more REEs from geothermal water. Neither the REE fractionation nor the Ce anomaly seems to be associated with Fe–Mn phases in the sinters. The fourth tetrads of some sinters display weak W-type (concave) effects. In contrast, the third tetrads present large effects in some sinters due to positive Gd anomalies. The origin of the positive Eu anomalies in some sinters seems to be caused by preferential dissolution of feldspars during water–rock interaction. The complexing ligands in geothermal water may contribute significantly to the fractionation of REEs in sinters. The dominant CO_3^{2-} and HCO_3^- complexing in geothermal water favors enrichment of heavy REEs in calcareous sinters.

1. Introduction

The Tibetan Plateau is a geothermally active region. According to incomplete statistics, there are at least 354 geothermally active areas on the Tibetan Plateau (Tong et al., 1981). Among them 129 show reservoir temperatures higher than 150 °C (Guo et al., 2009). Accompanied by a large number of geothermal waters, geothermal sinter deposits are widely distributed (Tong et al., 1981; Yao et al., 1986). Since the 1970s many studies have focused on the geothermal sinters on the Tibetan Plateau, including investigations of the fabrics (Zhao et al., 2008), mineral composition (Tong et al., 1981; Shen, 1986; Yao et al., 1986; Zentmyer et al., 2008; Zhao et al., 2010a), major chemical composition (Tong et al., 1981; Shen, 1986; Yao et al., 1986; Zhao et al., 2010a; Niu et al., 2013), trace element geochemistry (Zhao et al., 2007, 2010a), Si–C–O isotopes (Zhao et al., 2006, 2010a; Zentmyer et al., 2008), Sr–Nd isotopic composition (Zhao et al., 2006; Zentmyer et al., 2008), and ^{14}C, electron spin resonance (ESR) and uranium-series ages (Shen, 1986; Chen et al., 1992; Wang, 1992; Zentmyer et al., 2008; Zhao et al., 2010b; Gao et al., 2013). However, very little is known about the rare earth elements (REEs) in the various sinters (Li, 2002; Zhao et al., 2007, 2010a; Niu et al., 2013).

In general, sinters are deposits from geothermal water. They do not only reflect the chemical composition of geothermal water, but also give important information about host rocks of geothermal water and upstream channel rocks. They also elucidate water–rock interaction processes (Johannesson et al., 1997; Yokoyama et al., 1999; Fouke et al., 2000; Möller, 2000, 2002; Möller et al., 2006; Zhao et al., 2006, 2007; Siebert et al., 2014). Furthermore, the occurrences of geothermal deposits can reflect various episodes of hydrothermal and tectonic activities and extensional fault systems (Li, 2002; Zentmyer et al., 2008). Therefore, the characteristic features of sinters on the Tibetan Plateau, with its intense Cenozic tectonic activity, are worth investigating.

There is a general consensus about the mobility of the REEs during hydrothermal activity, but the fractionation of REEs resulting from such activity is still disputed (Xiong and Zhai, 1991; Haas et al., 1995; Migdisov et al., 2009; Feng et al., 2011; Williams-Jones et al., 2012; Migdisov and Williams-Jones, 2014).

In addition, the presence of a lanthanide tetrad effect is well confirmed by laboratory experiments (Fidelis and Siekierski, 1966; Peppard et al., 1969), but the existence, significance and origin of the lanthanide tetrad in geological materials are still matters of debate (Wood, 1990; Yurimoto et al., 1990; McLennan, 1994; Byrne and Li, 1995; Bau, 1997; Pan, 1997; Masau et al., 2000; Feng, 2010; Feng et al., 2011; Monecke et al., 2011).

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In recent decades, many investigators have focused on the lanthanide tetrad effect in highly evolved granitic systems because the tetrad effect can be used there as a geochemical indicator to constrain the evolution of igneous and hydrothermal systems (Masuda and Ikeuchi, 1979; Masuda et al., 1987; Bau, 1996; Irber, 1999; Jahn et al., 2001; Monecke et al., 2002, 2007, 2011; Zhao et al., 2010c).

The lanthanide tetrad effect has been documented in marine sediment systems, such as carbonate rocks and corals (Kawabe et al., 1991, 1998; Mazumdar et al., 2003; Tanaka et al., 2003; Akagi et al., 2004; Yamamoto et al., 2004), chert (Minami et al., 1998) and hydrogenetic marine ferromanganese crusts (Bau, 1996), and these studies have advanced our understanding of the incorporation of REEs and yttrium (REY) from seawater into marine sediments. In recent years, the lanthanide tetrad effect has been interpreted as a result of REE mobilization, transfer, precipitation, and redistribution under weathering conditions (Takahashi et al., 2002; Feng, 2010; Feng et al., 2011).

Although geothermal sinter deposits in terrestrial environments are related to water–rock interaction, little is known, as far as we know, about the development of lanthanide tetrad effects.

The objectives of the present study were to investigate (1) the characteristic features of REEs in various sinters; (2) the correlations of the REEs with other elements in sinters; (3) the lanthanide tetrad effect and other fractionation behavior of REEs in sinters; and (4) hydrogeological and hydrochemical implications of REEs in sinters. This work could shed light on REE behavior in various natural environments.

2. Geological setting and sample collection

Two geochemical regions on the Tibetan Plateau were investigated from which eleven sinter samples were collected (Fig. 1). One region is located in the north of the Yarlung Zangbo suture zone. It includes the Yangbajing (Yangbajain) and Yangyi geothermal fields and the Riduo geothermal hot spring.

The Yangbajing geothermal field is the most famous and important one on the Tibetan Plateau. It is approximately 87 km northwest of Lhasa (Fig. 1) and is located in a SW–NE trending terrigenous fault basin developed in the Cenozoic Era. The basin is bordered by the Nyainquentanglha Range to the northwest and the Tangshan Range to the southwest. The Yangbajing geothermal field is a typical convective system with a magmatic heat source (Dor Ji and Zhao, 2000). It consists of shallow and deep reservoirs. The shallow one, at depths less than 450 m, has temperatures of 150–165 °C. The deep reservoir can be subdivided into two parts: the upper part, at depths of 950 to 1336 m and a temperature 251 °C, and the lower part, below a depth of 1850 m, with temperatures as high as 329 °C. The shallow thermal water is a mixture of deep thermal water and cold groundwater (Dor Ji and Zhao, 2000; Zhao et al., 2000; JICA and TEPC, 2006). The first geothermal well and thermoelectric power plant in the Yangbajing geothermal field were completed in 1976 and 1977, respectively. Sinter samples YBJ-1 and YBJ-2 were collected from the scaling of pipelines carrying geothermal water from 340 m depth/120–125 °C and 300 m depth/118 °C, respectively (Fig. 2A and B).

The Yangyi geothermal field is located 50 km south of the Yangbajing geothermal field (Fig. 1). In this field, Miocene volcanic activity is strong; the field is igneous-related (Li et al., 1994; Guo, 2012). The highest measured well temperature at Yangyi geothermal field is 207 °C (Guo, 2012). During geothermal field exploration, some geothermal wells were drilled. Samples YBJ-6A and YBJ-6B were collected from sinter deposited on a cobble near the mouth of the geothermal well (Fig. 2C). YBJ-6A is from the porous and soft surface layer and is greenish gray (Gray 6/1; Munsell chart color, dry), whereas YBJ-6B is from a well-crystallized and hard layer colored pale yellow (2.5Y 8/3; Fig. 2D). From the same site, sample YBJ-6C was collected from a soft, slimy and hydrous deposit (Fig. 2E). The surface was covered by some slime of circular extension which might have been produced by microorganisms (Fig. 2E).

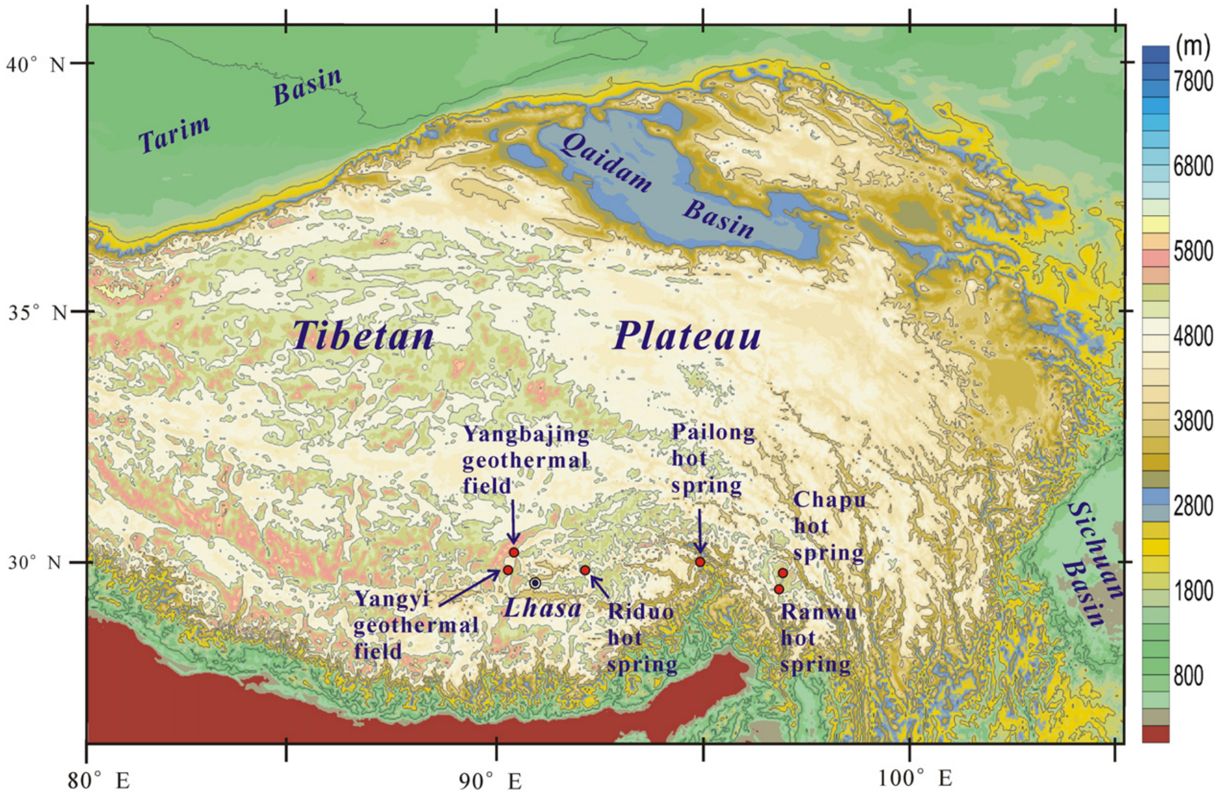

Fig. 1. Topographic sketch map of the study area and sampling sinters.